

# Experimental investigations for trapping oxygen gas in saturated porous media for in situ bioremediation

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**Abstract.** Oxygen is often the rate-limiting factor in aerobic in situ bioremediation. This paper investigates the degree to which air or oxygen gas can be emplaced into the pore space of saturated porous media and provide a significant mass of oxygen. Column experiments were performed to test three emplacement methods: direct gas injection, injection of water supersaturated with gas, and injection of a hydrogen peroxide solution. The direct gas injection method fills 14–17% of the pore space with trapped gas. Water supersaturated with gas fills 18–27% of the pore space with a trapped gas phase, and hydrogen peroxide solution injections emplaces trapped gas in 17–55% of the pore space. In addition to supplying oxygen, gas entrapment causes a decrease in hydraulic conductivity which could be an advantage by decreasing the flow of contaminants offsite. The relative hydraulic conductivity of porous media with a trapped gas volume of 14–55% was 0.62–0.05.

## 1. Introduction

Alternative methods are needed for introducing oxygen into groundwater for aerobic in situ bioremediation of contaminants. In situ bioremediation is often limited by the amount of oxygen available to the microorganisms in the subsurface. To degrade a simple hydrocarbon (e.g., benzene), approximately 3.1 times more oxygen than contaminant in mass/volume is necessary to meet the stoichiometric requirements. Since the solubility of oxygen in water is low, it is difficult to significantly increase the oxygen mass in a contaminated aquifer by dissolving the oxygen in water first before transferring it to the aquifer. Twenty-eight times more oxygen per volume can be stored in the gas phase than can be dissolved in water, assuming equilibrium based on Henry's law at 15°C.

We are investigating whether a wall or zone of trapped gas bubbles can be emplaced into an otherwise-saturated porous medium and provide a substantial source of oxygen for bioremediation of contaminated groundwater (Figure 1). If 15% of the pore space can be filled with oxygen gas, 20 times more oxygen will be emplaced compared to the case in which oxygen is dissolved in the pore water in equilibrium with air. Once a wall or zone of oxygen bubbles is emplaced into an aquifer, the oxygen will be dissolved by the water and be potentially available for use by microorganisms in biodegradation. When the oxygen is used up, it can be emplaced again. This cycle may be repeated until the contaminant is degraded to levels that meet the regulatory requirement. Because trapped gas emplacement does not require continuous injection, a bubble wall or zone may be constructed using modified sampling equipment (e.g., a Hydropunch™ or Geoprobe™), which will allow for much

closer spacing of injection points than injection through a well casing. Here we refer to oxygen because it is the gas that is most widely needed for bioremediation of contaminated groundwater, but other gases, such as hydrogen and methane, which have been shown to be effective in remediation of contaminated groundwater, could also be introduced into an aquifer by emplacement of a trapped gas phase.

### 1.1. Volume of Trapped Gas

Gas can be trapped in porous media because of the immiscible displacement of a gas by a liquid leaving a residual saturation of the gas behind or from exsolution of the gas from the liquid due to either supersaturation or a chemical reaction. In our study, gas is the nonwetting phase in water-wet porous media. The forces that determine the residual saturation of a nonwetting phase in a porous media are capillary, viscous, and buoyancy forces. The capillary forces are proportional to the interfacial tension between immiscible fluid phases and the wettability of the solid phase by a fluid. The viscous forces are proportional to the permeability of the media and the pressure gradient, and buoyancy forces are proportional to the density differences between fluids. A nonwetting phase can be trapped when the capillary forces are greater than either the viscous or buoyancy forces.

**1.1.1. Immiscible displacement.** A residual saturation of a nonwetting phase due to immiscible displacement has been studied extensively in many fields. In the field of soil science a residual saturation has been studied to understand the hydraulic effects of trapped gas in porous media due to water table fluctuations. In the petroleum engineering field the recovery of the maximum volume of oil from an oil reservoir when displacing the oil by water depends on knowledge of residual saturation. And more recently, in the field of hazardous waste, information on residual saturation has been sought to determine how to clean up organic liquids that have contaminated groundwater.

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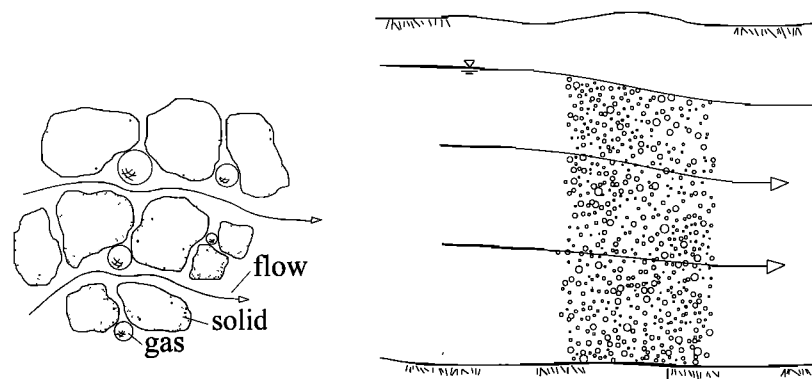


Figure 1. The pore scale and field scale conceptual model of the bubble wall.

Studies of trapped gas in porous media due to water table fluctuations have shown that a significant volume of gas can be trapped (typically 10–20% of the pore space), although the volume can vary substantially depending on various parameters of the porous media (see Table 1). Glass beads, sand, loam, and clay were among the types of porous media that were tested in these experiments.

A few representative experiments in petroleum recovery research and hazardous waste cleanup also show that the maximum residual saturation of a trapped nonwetting phase can be significant (see Table 2). Differences in the nonwetting fluids used can be accounted for by using dimensionless numbers [Morrow and Songkran, 1981]. The dimensionless numbers of interest are the capillary number (viscous/capillary forces) and the bond number (buoyancy/capillary forces). At large capillary numbers, when the nonwetting phase is gas versus oil, the volume of trapped gas is slightly smaller than the volume of trapped oil [Morrow *et al.*, 1985]. Plots of the bond number versus residual saturation shows that a water-air fluid pair gives a slightly smaller (1.5%) residual saturation compared to a water-oil fluid pair [Morrow and Songkran, 1981; Morrow *et al.*, 1985].

**1.1.2. Exsolution.** Many studies have also been performed to understand bubble nucleation and bubble growth in porous media due to pressure depletion in typical oil-recovery methods [Hunt and Berry, 1956; Li and Yortsos, 1994, 1995a, b]. Bubbles can exsolve out of the water phase in situ if the gas dissolved in the water is supersaturated. Supersaturation can occur if there is a decrease in pressure or an increase in temperature. Experiments of Li and Yortsos [1995a], where water supersaturated with carbon dioxide was introduced into a glass micromodel, found that up to 20% of the pore space was filled with a gas phase before bulk gas started flowing out of the outlet. Gas can also be generated in situ by the decomposition of organics by microbes in the soil or by an inorganic reaction creating a gaseous byproduct. Reynolds *et al.* [1992] measured up to 32% trapped gas in an otherwise-saturated peat where the gas was generated in situ by microbes. The bubbles will mobilize if the viscous or buoyancy forces are greater than the capillary forces.

## 1.2. Parameters That Affect the Volume of Trapped Gas

**1.2.1. Immiscible displacement.** The literature on trapped air in porous media due to water table fluctuations has shown that the volume of trapped gas is dependent on the solubility of the gas in the liquid phase and therefore on the

temperature and pressure [Christiansen, 1944]. Below the water table the pressure and thus the solubility of a gas will increase with depth. An increase in the concentration of dissolved gas with depth will cause a slow diffusion of dissolved gas upwards through the water because of the concentration gradient. The volume of trapped gas will slowly decrease as the gas dissolves into the aqueous phase in order to maintain an equilibrium between the gas and aqueous phase concentrations. The volume of trapped gas will also decrease with time due to the radius of curvature of the gas bubble [Adam *et al.*, 1969]. The radius of curvature creates an increase in pressure in the gas bubble causing the concentration of gas in the bubble to increase. The increased concentration in the gas bubble creates a concentration gradient causing the gas to slowly diffuse out of the bubble into the surrounding water and then upwards toward the surface of the water table. An increase in pressure with depth will also cause a mass of trapped gas to have a smaller volume with depth. The volume of gas trapped has also been shown to be affected by the infiltration rate, the initial soil moisture content [Fayer and Hillel, 1986], and the pore structure [Peck, 1969].

Many experiments have been performed in petroleum recovery research and hazardous waste cleanup studies to determine the parameters that will influence the residual saturation of a nonwetting phase. The capillary number and the bond number can be used to determine the effect of the viscous and buoyancy forces relative to the capillary forces on the volume of residual nonwetting phase [Morrow and Songkran, 1981; Wilson *et al.*, 1990]. At large capillary and bond numbers, the volume of nonwetting phase residual decreases as the capillary/bond number increases. Below a critical value, the residual saturation is independent of the capillary and bond numbers. This scenario is typical of groundwater systems where gas or oil is the nonwetting phase [Wilson and Conrad, 1984]. When the bond number and capillary number are below their critical values, capillary forces dominate and the residual saturations are independent of the direction of wetting phase flow relative to buoyancy forces [Morrow and Songkran, 1981].

Residual saturation has also been shown to be dependent on the structure of the pore space [Wardlaw, 1982; Chatzis *et al.*, 1983]. Larger numbers of poorly connected pores and increase in pore size variability correlate with increase in residual saturation [Coskun and Wardlaw, 1994]. The aspect ratio of pore to throat will also affect the volume trapped; the greater the aspect ratio, the larger the volume trapped [Wardlaw, 1982; Chatzis *et al.*, 1983]. The fines content (even 3% clay and silt)

**Table 1.** Review of Soil Science Literature on Trapped Gas Due to Water Table Fluctuations

Soil Type	Trapped Gas, % of Pore Space	Porosity, % of Bulk Volume	Relative Hydraulic Conductivity, $K_{\text{trap gas}}/K_{\text{sat}}$	Type of Experiment	Method for Introducing Gas Phase	Reference
Agricultural soils	4.8-22	...	...	laboratory	unsaturated soil wetted from below	Smith and Browning [1942]
Hesperia sandy loam	15-40	...	0.22-0.5	laboratory	unsaturated soil wetted from below	Christiansen [1944]
Hanford soil	12-21	35-44	0.5	laboratory	unsaturated soil wetted from above	Orlob and Radhakrishna [1958]
Sintered glass beads	16.4	...	...	laboratory	unsaturated soil wetted from below	Poulavassilis [1970]
Consolidated clays	4.8-6.7	62	...	laboratory	unsaturated soil wetted from below	Adam et al. [1969]
Fine sandy loam to loamy sand	4.3-12.6	50	...	field	unsaturated soil wetted from above	Fayer and Hillel [1986]
Los gatos gravelly loam	12	43	0.1	field	unsaturated soil wetted from above	Constanz et al. [1988]
Diablo sandy loam	4	45	0.21	field	unsaturated soil wetted from above	Constanz et al. [1988]
Olympic sand	19	36	0.2	field	unsaturated soil wetted from above	Constanz et al. [1988]
Aiken loam	12	51	0.2	field	unsaturated soil wetted from above	Constanz et al. [1988]
Aiken aggregates	6.9	69	...	laboratory	unsaturated soil wetted from below	Stonestrom and Rubin [1989]
Oakley sand	12.6	37	...	laboratory	unsaturated soil wetted from below	Stonestrom and Rubin [1989]
Loam	approximately 8-10	approximately 43	0.04-0.06	laboratory	unsaturated soil wetted from above	Faybishenko [1995]

can also cause a significant increase in the residual (from 17% to 25%) due to the fine particles flocculating at the interface [Mace and Wilson, 1992].

Experiments using glass beads have shown that the residual nonwetting phase saturation is not dependent on the grain size unless the matrix is so fine that the wetting phase cannot be displaced initially by the nonwetting phase [Chatzis et al., 1983; Wilson et al., 1990]. The residual saturation was also shown not to be a function of the composition of the beads when two different bead sizes were used where the percentage of each used was varied [Chatzis et al., 1983]. However, the residual saturation did increase slightly with an increase in the distribution of bead sizes when more than two bead sizes were used (16.4% versus 14%) [Chatzis et al., 1983]. Residual saturation does not correlate with the hydraulic conductivity or organic carbon content [Wilson et al., 1990].

Residual saturation also depends on the number of pore volumes of the wetting phase that flow through the porous medium when the nonwetting phase is soluble in the wetting phase and they are not in equilibrium [Morrow and Songkran, 1981; Morrow et al., 1985].

**1.2.2. Exsolution.** The volume of gas trapped in porous media by exsolution of gas out of the liquid phase is dependent on the number of sites where the bubbles can nucleate. The nucleation of gas bubbles in porous media is thought to occur within cavities on the pore surface [Li and Yortsos, 1994]. The onset of nucleation occurs when the local supersaturation exceeds the capillary pressure at a site. The critical supersaturation for activation is  $KC - P_i \geq 2\gamma/W$  where  $K$  is the solubility constant,  $C$  is the local concentration,  $P_i$  is the liquid pressure,  $\gamma$  is interfacial tension, and  $W$  is the half width of the mouth of a conical cavity [Li and Yortsos, 1994]. The rate at which bubbles are formed increases rapidly with increasing supersaturation [Hunt and Berry, 1956]. If the supersaturation occurs because of a decrease in pressure, the total volume of gas increases with an increase in the pressure decline rate as a result of an increase in the number of nucleation sites [Hunt and Berry, 1956].

The volume of gas trapped is also dependent on the growth of the gas bubbles following nucleation. The rate at which the bubbles grow is dependent on the mass transfer of the gas through the liquid into the gas bubbles. The mass transfer of the gas will occur from diffusion due to a concentration gradient and advection if the liquid is flowing. Geometric and topological features affect the volume of gas trapped because of the length of the diffusion and advection paths. The diffusion of the gas through the bubble wall will depend on the surface tension of the two fluids and any organic compounds that may be on the bubble wall [Manley, 1960; Li and Yortsos, 1995a, b]. In a porous media where capillary effects are present, the growth of gas bubbles occur in two essential steps: a pore-filling step and a pressurization step [Li and Yortsos, 1995b]. Following nucleation of a gas bubble, the bubble grows, filling the pore body. When a pore body is filled with a gas phase, the gas bubble can only grow larger into the surrounding pores when the pressure inside the bubble surpasses the capillary threshold pressure of a surrounding throat. These two steps can then be repeated.

### 1.3. Effects of Trapped Gas on Hydraulic Conductivity

The cause of variations in the hydraulic conductivity of soil with time in the zone where the water table fluctuates was unknown until Christiansen [1944] proved that entrapped air

**Table 2.** Review of Petroleum Recovery and Hazardous Waste Literature on Residual Saturation due to Immiscible Displacement

Soil Type	Maximum Residual Saturation, % of Pore Space	Wetting Phase	Nonwetting Phase	Porosity, % of Bulk Volume	Relative Hydraulic Conductivity	Reference
Glass beads	14.25 ± 0.25	oil	air	...	0.63 ± 0.02	<i>Morrow and Songkran</i> [1981]
Glass beads	14 ± 19	oil	air	...	...	<i>Chatzis et al.</i> [1983]
Glass beads	14–16	water	oil	...	approximately 0.52	<i>Morrow et al.</i> [1985]
Sandstone	27–43	water	oil	16–27	0.06–0.41	<i>Chatzis and Morrow</i> [1984]
Sand	14–29	water	oil	33–38	...	<i>Wilson et al.</i> [1990]

was responsible for this effect. The hydraulic conductivity has been shown to be reduced because of a trapped gas phase yielding a relative hydraulic conductivity ( $K_{\text{trap gas}}/K_{\text{sat}}$ ) of 0.04–0.5 (Table 1).

The effect of a residual nonwetting phase on the hydraulic conductivity of a wetting phase through porous media has also been studied in the petroleum recovery and hazardous waste cleanup literature. Relative permeabilities were shown to be independent of whether the trapped phase was oil or gas [*Morrow et al.*, 1985]. The relative hydraulic conductivity ranges from 0.06 to 0.63 because of a residual saturation filling 14–43% of the pore space (Table 2). *Morrow et al.* [1985] have shown that the volume of residual nonwetting phase saturation, rather than its detailed structure or distribution in the pore space, determines the wetting phase hydraulic conductivity.

#### 1.4. Objectives of This Study

The goals of this study were to determine (1) the volume of gas that can be emplaced into otherwise-saturated porous media using alternative methods of emplacement and (2) the effects of trapped gas on the hydraulic conductivity of the porous medium. Laboratory experiments were performed to investigate these objectives.

## 2. Emplacement Methods

Three methods for emplacement of trapped gas into fully saturated porous media are considered here: direct gas injection, injection of water supersaturated with gas, and injection of a hydrogen peroxide solution.

### 2.1. Direct Gas Injection

The direct gas injection method adds air or oxygen gas into a saturated porous medium from below. Once a substantial volume of gas is trapped in the porous medium, the injection of gas can be stopped. This method is similar to air sparging, but the objectives are different. In air sparging the goal is to have air channels continually traveling through the water to cause mass transfer of volatile contaminants and/or oxygen between the water and the gas phase. In direct gas injection the goal is to trap as much of the gas as possible in the pore spaces, stop the injection, and allow time for the gas to dissolve into the water to be available for bioremediation.

In a field application of the direct gas injection method, water will initially be displaced upward by gas injected below the water table. After the gas injection is turned off, water will tend to flow back into the area. The gas will be displaced by water from above and from the sides because of the buoyancy

instability created by emplacing a less dense fluid below a denser fluid. Gas will be forced either to move upward through the water, causing a counterflow of the gas and the water, or to move laterally or downward. The volume of gas trapped because of the direct gas injection method can be related to the immiscible displacement studies.

### 2.2. Injection of Water Supersaturated With Gas

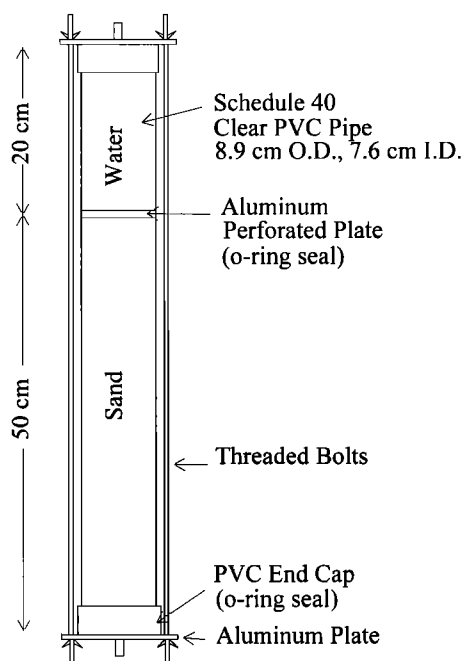
Gas can exsolve out of water supersaturated with the gas. Water can be supersaturated with air or oxygen gas by dissolving the gas in water at high pressure and then decreasing the pressure. If pressurized water that has been saturated with gas is injected into an aquifer, the pressure will decrease as the water moves into the aquifer and the gas will come out of solution in situ in the form of bubbles that can be trapped in the porous medium. The mobilization of these bubbles will depend on the strength of the buoyancy and viscous forces relative to the capillary forces. The injection of water supersaturated with gas can be related to the literature on bubble nucleation and growth.

### 2.3. Injection of a Hydrogen Peroxide Solution

Hydrogen peroxide decomposes to oxygen and water and has been used to increase the mass of oxygen in groundwater for bioremediation. The rate of decomposition of hydrogen peroxide increases with a higher concentration of catalytic metals such as Fe and Mn and with a higher population density of catalase positive microorganisms [*Pardieck et al.*, 1992]. In a field study hydrogen peroxide was shown to decompose rapidly in the subsurface [*Huling et al.*, 1990]. The concentration of oxygen in the water reaches supersaturation levels causing the oxygen to exsolve out of the water in the form of bubbles. The sites of nucleation of the bubbles will be similar to any process that causes the water to be supersaturated with a gas. The mobilization of these bubbles will also depend on the strength of the buoyancy and viscous forces relative to the capillary forces. The research on the nucleation and growth of gas bubbles in situ in porous media [*Hunt and Berry*, 1956; *Li and Yortsos*, 1995a, b] will be applicable to this method as well.

## 3. Laboratory Experiments

Column experiments were performed to determine the volume of gas that can be trapped throughout a saturated porous media for the three methods of emplacement described above. The effect of this trapped gas on the hydraulic conductivity of the porous media was also determined.



**Figure 2.** Schematic of the column used for testing methods for emplacement of gas into saturated porous media.

### 3.1. Column Design

The column was made of transparent schedule 40, PVC pipe with an inside diameter of 7.6 cm (3.0 inches) and wall thickness of 0.64 cm (0.25 inches) (Figure 2). The pipe was cut into two sections. The sand was packed in the lower section of the column which is 50 cm long and has an internal volume of 2.3 L. The upper section of the column was designed to hold a reservoir of water. It is 20 cm long and has an internal volume of 0.9 L. The upper and lower sections of the column are separated by a 0.64 cm (0.25 inch) thick aluminum perforated plate. The column was capped on top and bottom with PVC end caps. Two layers of expanded aluminum were placed in the bottom end cap to aid in dispersing the injection fluid and a nylon screen was placed at both ends of the sand pack to retain the medium. The entire assembly was held together by clamping aluminum plates at both ends of the column with four threaded bolts that run the length of the column. The column was sealed by O-rings on both end caps and an O-ring on the perforated plate to seal the connection between the lower and upper sections of the pipe.

### 3.2. Porous Media

Three different size fractions of fine to coarse silica sand were used in the experiments. The sand (trade name Accusand®) is sold by Unimin Corporation, Le Sueur, Minnesota. The porous medium is from a natural site and has been pre-washed and presieved. It is a very uniform sand with a high sphericity and a high degree of consistency from batch to batch (Table 3). The grades of sand used are 12/20 (coarse), 30/40 (medium), and 40/50 (fine), where the first number is the sieve size through which all the sand passes and the second number is the sieve size through which none of the sand passes. A summary of the hydraulic, physical, and chemical properties of the sand are in Table 3, with further details provided by Schroth *et al.* [1996]. The sand was washed prior to use to

**Table 3.** The Physical and Chemical Properties of Accusand®

	Accusand Grade		
	12/20	30/40	40/50
<i>Physical Properties</i>			
Particle diameter $d_{50}$ mm	1.105	0.532	0.359
Uniformity coefficient $d_{60}/d_{10}$	1.231	1.207	1.200
Particle sphericity	0.9	0.9	0.9
Particle density, g/cm <sup>3</sup>	2.665	2.665	2.663
$K_{sat}$ , * cm/min	34.7	7.7	3.5
<i>Chemical Analyses</i>			
Cation exchange capacity (CEC), meq/100 g	0.60	0.62	0.67
Total iron, %	0.931	0.765	0.558
Iron oxides, %	0.036	0.034	0.03
Organic carbon, µg/g	0.03	0.03	0.03
Total cadmium, µg/g	<7.0	<7.0	<7.0
Total copper, µg/g	<14.0	<14.0	<14.0
Total lead, µg/g	<5.0	<5.0	<5.0
Total manganese, µg/g	51.6	40.3	34.1
Total zinc, µg/g	9.95	7.10	6.18

Properties from Schroth *et al.* [1996].

\*Hydraulic conductivity determined in this study.

remove any fines that may have been generated during shipping and was oven dried at 50°C for a minimum of 24 hours.

The sand was packed into the column using a wet-packing procedure. Small increments of water were added into the column prior to adding sand to minimize the separation of sand sizes due to differences in settling rates as the sand fell into the column. As the sand was added into the column, the sand was tamped down lightly. The column was packed to a porosity of 0.348 for the three different grades of sand. The total pore volume of the packed column was 787 cm<sup>3</sup>.

The sand was fully saturated by draining the column, injecting CO<sub>2</sub> gas from below to fill the pore spaces, and pumping from below two pore volumes of de-aired water into the column followed by two pore volumes of water in equilibrium with air at 20°C. The volume of trapped gas within the pore space of the sand was measured gravimetrically by taking the difference between the weight of the fully saturated column and the weight of the column with trapped gas. The hydraulic conductivity of the porous medium was measured by the constant head method. The measurements have been adjusted to take into account the effects of the column fittings by measuring the hydraulic conductivity of the column with no sand and incorporating this correction into the results [Klute and Dirksen, 1986]. The hydraulic conductivity of the porous medium was measured before and after the gas was trapped to determine the relative hydraulic conductivity.

### 3.3. Experimental Procedures

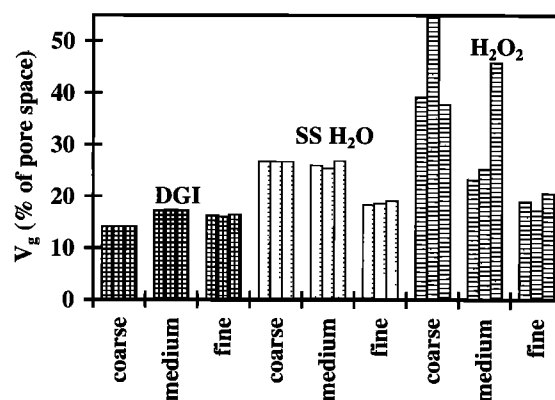
Three replicate experiments were performed for each emplacement method and sand type tested. Prior to each of these experiments, the column was fully saturated with water, the column was weighed, and the hydraulic conductivity of the fully saturated column was determined. After the gas was trapped in the pore space using the various different methods of emplacement, 300 mL (0.4 pore volumes) of water was allowed to flow through the column and out of the bottom port to eliminate any gas that was trapped in the bottom valve. The weight of the column and the hydraulic conductivity of the porous medium were measured again after the gas emplacement.

**3.3.1. Direct gas injection.** The direct gas injection method was implemented in the laboratory by injecting compressed air set at a constant gauge pressure of 0.34 atm (5 psi) into the injection port in the bottom of the column. After 60 s the gas injection was turned off, the valve on the bottom of the column was closed, and water infiltrated back into the porous medium from the upper reservoir. The water was assumed to be completely infiltrated back into the column when no more gas could be seen bubbling out of the porous medium into the water reservoir.

**3.3.2. Injection of water supersaturated with gas.** The method of injection of water supersaturated with gas was accomplished by supersaturating water with air in a pressure chamber. The water was pressurized up to a gauge pressure of 1.6 atm (23 psi) in order to increase the solubility of gas in water by a factor of 2.6. Air was dissolved in the water by sparging with compressed air and the excess gas was vented off. Fifteen liters (19.1 pore volumes) of the supersaturated water was injected from below into a fully saturated column at a gauge pressure of 1.6 atm (23 psi). As the water entered the column, the pressure decreased causing the gas to exsolve out of the water into the pore space. The pressure in the column was not measured directly, but it decreased with distance away from the injection point at the bottom of the column. The minimum pressure was higher than hydrostatic, and maximum gauge pressure was less than 1.6 atm. There is enough dissolved gas at solubility at a gauge pressure of 1.6 atm in 15 liters of water that when the pressure is decreased to 0.0 atm, 67% of the pore space could be filled with gas if all of the gas were retained in the porous medium.

**3.3.3. Injection of a hydrogen peroxide solution.** The hydrogen peroxide solution method was performed by injecting two pore volumes of a 2000-ppm solution of hydrogen peroxide from below into a fully saturated column. The column was then allowed to sit until the hydrogen peroxide decomposed enough to show signs of trapped gas throughout the pore space (approximately 48 hours). The column was repacked for each hydrogen peroxide experiment performed. The concentration of hydrogen peroxide necessary to cause a substantial volume of gas to be trapped will be variable depending on the chemistry of the porous medium. We chose to use a high concentration of hydrogen peroxide to obtain the largest volume of gas that could be trapped with this method, with excess gas observed to be bubbling out of the porous media in each experiment.

**3.3.4. Additional experiments.** An additional series of direct gas injection experiments were run to determine if the direction in which the gas is displaced from the porous medium and the direction of flow of the displacing water affect the volume of gas that can be trapped. The volume of gas trapped in the experiments where the flow of the gas was upward and water flow was downward (counterflow) will be compared to the volume of gas trapped when the gas and water are displaced either downward or upward. As discussed above, the likely scenario for direct gas injection in the field is that the gas will be moving upward in a counterflow to the water or the gas and the water will both be moving in a downward flow. Immiscible displacement experiments have typically displaced gas upward as water was pumped upward (upward flow displacement). To show how the results of our direct gas injection experiments compare to upward flow displacement experiments, we performed an experiment where the medium was initially fully saturated with water as the wetting phase, air was



**Figure 3.** Volume of trapped gas ( $V_g$ ) versus emplacement method and grade of sand tested. The emplacement methods are direct gas injection (DGI), injection of supersaturated water (SS  $H_2O$ ), and injection of a hydrogen peroxide solution ( $H_2O_2$ ). Each bar represents one experiment.

injected into the inlet port as the nonwetting phase, and then water displaced the air from below. The velocity of the water displacing the gas was varied for each experiment.

Experiments were also performed to determine the volume of trapped gas when there was a downward flow of both the gas (nonwetting phase) and the water (wetting phase). In these experiments, after the air injection was shut off, water infiltrated back into the column from the reservoir above but the port at the bottom of the column was opened to allow both the gas and water to flow downward. No gas was seen bubbling out into the reservoir above. The level of the water in the reservoir was held constant, and the water flux going into the column was measured to determine the velocity of the water. These experiments were run on the medium and fine sand.

Experiments were run to test whether the volume of gas trapped for the direct gas injection method was dependent on the duration of gas injection. The column was packed with the medium grade sand. Air was injected at a constant gauge pressure of 0.14 atm (2 psi) into the injection port in the bottom of a fully saturated column. After a set length of time, the gas injection was turned off, the valve on the bottom of the column was closed, and water was allowed to infiltrate back into the porous medium from the reservoir above. The length of time the gas was injected was varied between 1.5 and 12 min. The column was weighed before and after each experiment to determine the volume of gas trapped.

Another series of experiments tested whether the volume of gas trapped using the direct gas injection method was dependent on the injection pressure. These experiments were similar to those described above except that the gauge pressure of injection was varied between 0.10 and 0.68 atm (1.5 and 10 psi).

## 4. Results

### 4.1. Emplacement Method

The first series of experiments were performed to determine how much gas can be trapped using different methods of emplacement and grades of sand. All of the emplacement methods and grades of sand tested showed that a significant volume of gas can be trapped in the pore space of an otherwise-saturated porous medium (Figure 3). The direct gas injection method emplaced a trapped gas volume of 14–17% of the pore

space with slightly less in the coarse grade of sand compared to the medium and fine sands. The smaller volume of gas in the coarse sand may be a result of the smaller capillary forces due to larger pore throats and the larger viscous forces due to a higher hydraulic conductivity. Injection of supersaturated water filled 18–27% of the pore space with trapped gas with a smaller volume of gas trapped in the fine sands relative to the medium and coarse sands. Experimental replications for both the direct gas injection and the supersaturated water injection methods showed a high consistency of results. The volume of gas trapped from injection of the hydrogen peroxide solution was more variable from experiment to experiment and for the different grades of sand ranging from 17% to 55%.

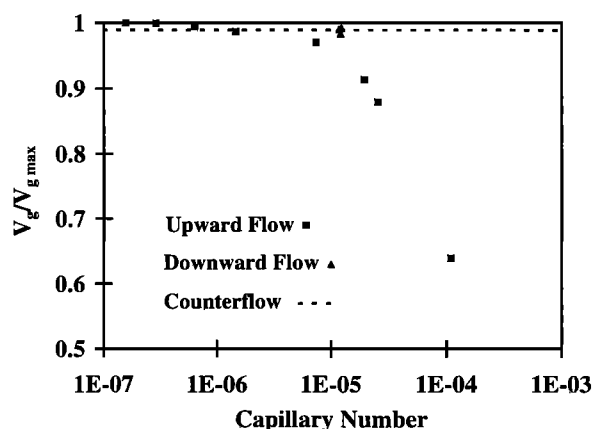
In both the supersaturated water method and hydrogen peroxide injection method, larger volumes of gas were trapped in the coarse and medium sand compared to the direct gas injection method. In these methods, gas bubbles form in situ and may fill the smaller pore spaces that cannot be filled in the direct gas injection method because of capillary forces filling the smaller pore spaces with water. The fine sand does not show an increase in the volume of trapped gas for both the supersaturated water and the hydrogen peroxide injection methods. The reason for this is still unclear.

In the coarse sand the hydrogen peroxide solution method shows a larger volume of trapped gas than in the supersaturated water method. This result may be due to the differences in viscous forces between the two methods. In the hydrogen peroxide solution method, once the solution has been injected into the sand pack, there is no hydraulic gradient on the water and thus no viscous shear forces due to water movement. This may have allowed the gas to reside in pore spaces that would otherwise have filled with water if large viscous forces were present. In the supersaturated water injection the water is being injected into the sand pack with a large hydraulic gradient and thus the viscous forces are large as the gas is exsolving out of solution.

The variability in the results for the hydrogen peroxide experiments may be due to repacking the column with sand after each experiment. Different sand packs may have had a different number of sites for nucleation of the gas bubbles in situ or a slightly different amount of fines that could flocculate at the fluid-fluid interface, both of which could affect the volume of gas trapped.

#### 4.2. Direct Gas Injection: Direction of Displacement

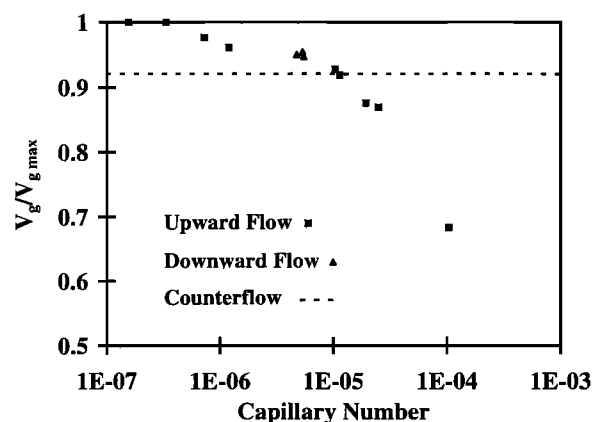
In the direct gas injection method the effect of the direction of displacement of the nonwetting fluid by the wetting fluid on the volume of gas trapped was determined. Typically, in immiscible displacement experiments the wetting phase flows upward displacing the nonwetting phase upward rather than a counterflow of the wetting and nonwetting phases as in the direct gas injection experiments. The results of this comparison are plotted as capillary number versus the volume of gas trapped normalized by the maximum volume of gas trapped (Figures 4 and 5). Capillary number is a ratio of viscous to capillary forces (darcy velocity  $\times$  viscosity of water/interfacial tension between the fluids). Experiments were run for both the medium and fine sand. The upward displacement results show a curve typical of immiscible displacement experiments where above a capillary number (the critical capillary number), the residual saturation decreases with an increase in the capillary number, but below the critical capillary number, the residual saturation is constant with capillary number. The critical capillary



**Figure 4.** Volume of trapped gas normalized by the maximum volume of trapped gas ( $V_g/V_{g\max}$ ) versus capillary number. Comparison of the method of displacement of the wetting and nonwetting phases for the direct gas injection method (counterflow) to an upward flow and a downward flow displacement (medium sand).

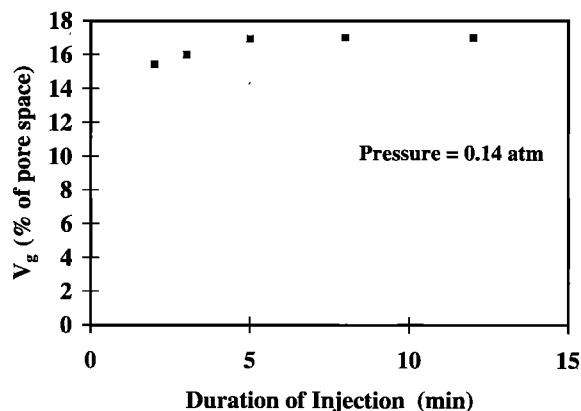
illary number for these experiments is approximately  $10^{-5}$ – $10^{-6}$ ; the critical capillary numbers for entrapment of oil as the nonwetting phase in sandstones are also on the order of  $10^{-5}$ – $10^{-6}$  [Chatzis and Morrow, 1984].

Experiments with a downward displacement for both the water and the gas are also plotted in Figures 4 and 5. The evidence that the gas was being displaced downward was that there was no gas seen bubbling through the water reservoir above the sand pack. There is only one value for the capillary number since the velocity of water flow was kept constant by infiltration from a constant head. The volume of trapped gas for downward displacement is similar to the volume of trapped gas for upward displacement with the same capillary number. This suggests that the effects of buoyancy are negligible in these experiments. Thus the bond number, a ratio of the buoyancy to capillary forces (intrinsic permeability of soil  $\times$  density difference between fluids  $\times$  acceleration of gravity/interfacial tension), must be below the critical value. The critical bond

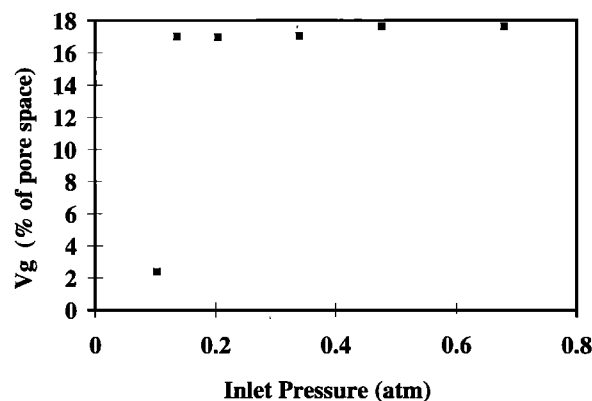


**Figure 5.** Volume of trapped gas normalized by the maximum volume of trapped gas ( $V_g/V_{g\max}$ ) versus capillary number. Comparison of the method of displacement of the wetting and nonwetting phases for the direct gas injection method (counterflow) to an upward flow and a downward flow displacement (fine sand).





**Figure 6.** Volume of trapped gas ( $V_g$ ) versus injection duration for direct gas injection method into medium grade sand.



**Figure 7.** Volume of trapped gas ( $V_g$ ) versus injection pressure for direct gas injection method into medium grade sand.

number is defined as the number where above it, the residual saturation decreases with an increase in the bond number and below it, where the residual saturation is constant with bond number. The bond number calculated for these experiments is on the order of  $10^{-4}$ – $10^{-5}$ ; the critical bond number for air as the nonwetting phase in water-wet glass beads is on the order of  $10^{-3}$  [Morrow and Songkran, 1981].

The results of the direct gas injection experiments are also plotted as a dashed line in Figures 4 and 5 where the displacing water infiltrates down from above and the gas is escaping upward, counterflow to the water. The capillary number cannot be plotted as one value because the velocity of the displacing water will be fast initially and will slow with time. The volume of trapped gas is on the same order as the volume of trapped gas below the critical capillary number for the upward displacement experiments for both grades of sand tested. In direct gas injection, gas will be displaced out in the field by counterflow or downward flow of the gas and water. The volume of gas trapped will be similar for both of these types of displacement. Similarly, immiscible displacement experiments where the displacement is upward can be directly compared to our experiments.

#### 4.3. Direct Gas Injection: Duration and Pressure of Injection

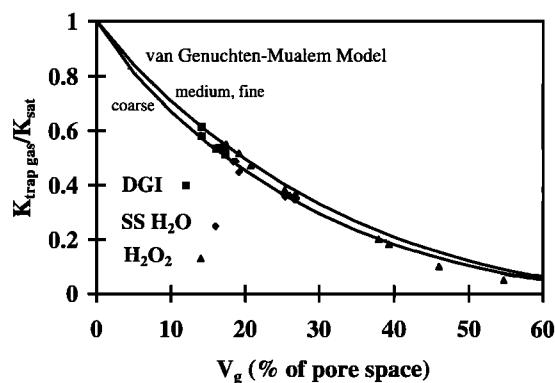
The duration of the injection time for the direct gas injection method was tested to see what effect it had on the volume of trapped gas. Our experimental results show that the volume of gas trapped was constant when the duration of injection was above a minimum value (Figure 6). The minimum duration corresponds to an injection of approximately 30 pore volumes of gas.

The pressure of injection for the direct gas injection method was also tested to see what effect it had on the volume of gas that was trapped. The volume of gas trapped was constant above a minimum pressure of injection of 0.07 atm (1 psi) above the hydrostatic head (a gauge pressure of 0.07 atm (1 psi) at the bottom of the column) (Figure 7). Below this critical pressure and above the pressure for air to move into the porous medium (a sum of the hydrostatic pressure and the air entry pressure), the gas flowed in channels because of the Saffman-Taylor instability [Saffman and Taylor, 1958]. The air entry pressure for this sand is approximately 0.012 atm as determined by Schroth *et al.* [1996]. When the gas flowed in

channels through the column, the volume of gas that was trapped was reduced.

#### 4.4. Effect of Trapped Gas on Hydraulic Conductivity

When gas is trapped in an otherwise-saturated porous medium, the relative hydraulic conductivity decreases as the volume of gas trapped increases. Our experiments show that the relative hydraulic conductivity ranges from 0.62 to 0.05 for a trapped gas volume filling 14–55% of the pore space, respectively (Figure 8). The van Genuchten-Mualem model of the unsaturated conductivity function [van Genuchten, 1980] calibrated by main drainage water retention data for the three grades of sand [Schroth *et al.*, 1996] is also plotted in Figure 8. Our experimental data match these model results quite well. Our conclusion from these results is that the relative hydraulic conductivity is dependent on the volume of the gas phase, and independent of both the methods of emplacement and whether the gas is trapped or situated in connected paths to the atmosphere as is the case in main drainage water retention experiments performed by Schroth *et al.* [1996].



**Figure 8.** Relative hydraulic conductivity of the porous medium with trapped gas ( $K_{\text{trap gas}}/K_{\text{sat}}$ ) versus the volume of trapped gas ( $V_g$ ) for the three different methods of emplacement used in the experiments. Comparison between the van Genuchten-Mualem model of unsaturated conductivity calibrated using water retention data for the three grades of sand and the experimental results of trapped gas emplacement.



## 5. Summary and Conclusions

We have investigated the emplacement of a trapped gas phase into saturated porous media as an alternative method for introducing oxygen into groundwater for in situ bioremediation. Laboratory experiments have been performed to test three methods for emplacement of trapped gas into porous media: direct gas injection, supersaturated water injection, and hydrogen peroxide solution injection. All three types of experiments aimed at evaluating these methods of emplacement of trapped gas showed that in a small-scale column, a significant volume of gas can be trapped (14–55% of the pore space). Supersaturated water injection and hydrogen peroxide solution injection trapped the largest volume of gas (23–55% of the pore space) in both the medium and coarse grades of sand. The fine sand trapped approximately the same volume of gas for all three emplacement methods tested (16–21% of the pore space).

Acting on a gas phase in a water-wet porous medium are capillary, buoyancy, and viscous forces. The capillary forces act to trap the gas phase from going through the pore throats, whereas the buoyancy and viscous forces act to move the gas phase out of the medium. Morrow and Songkran [1981] have shown that when the bond number (buoyancy/capillary forces) for a gas phase in water-wet porous media is small relative to the critical bond number, the capillary forces hold the gas phase in the interstitial pore spaces over the buoyancy forces [Morrow and Songkran, 1981]. Our experiments comparing upward flow and downward flow displacement of the gas phase by water also showed that the buoyancy forces were negligible compared to the capillary forces for our system. At the same capillary number the volume of gas trapped was similar for both upward and downward flow displacement methods.

During entrapment of the gas phase the viscous forces will vary depending on the method of emplacement. In the direct gas injection method the gas phase will be entrapped after the gas injection is turned off and the water flows back into the porous medium. The flow of water back into a typical porous medium is slow and thus the viscous forces will be small relative to the capillary forces (small capillary number). During entrapment of the gas phase in the supersaturated water injection method the viscous forces may be large and will act to displace the gas phase out of the medium, but this displacement will be counteracted by the gas bubbles growing in situ. In the hydrogen peroxide method the viscous forces during entrapment of the gas phase will be small and will not act to decrease the volume of gas trapped. After entrapment of the gas phase from all three methods of emplacement the viscous forces, due to typical groundwater velocity, will be small relative to the capillary forces, and thus it will be difficult to mobilize the gas phase once it is emplaced. The viscous forces necessary for mobilization of a nonwetting phase that has been trapped are significantly greater than the viscous forces needed to prevent entrapment of the nonwetting phase initially [Morrow and Songkran, 1981; Morrow et al., 1985].

Emplacement of a trapped gas phase into porous media will reduce the hydraulic conductivity. Our experiments measured a relative hydraulic conductivity of 0.62–0.05 for a trapped gas volume of 14–55% of the pore space, respectively. This reduction can be an advantage when oxygen gas is emplaced at the site of contamination since the flow of contaminants off site will be decreased. The effects of a trapped gas phase on the hydraulic conductivity are well described by the van Genuchten-Mualem model of unsaturated hydraulic conductivity calibrated by water retention measurements using standard methods. The relative hydraulic conductivity was shown to be dependent on the volume of gas phase in the pore space (trapped or open to the atmosphere) and independent of the method of emplacement. Morrow et al. [1985] similarly found that the hydraulic conductivity was dependent on the magnitude of the nonwetting phase (oil) saturation rather than its detailed structure and distribution.

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